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THE EVALUATION OF MATRIX ELEMENTS WITH GENERALIZED SPHERICAL GA--ETC(U)
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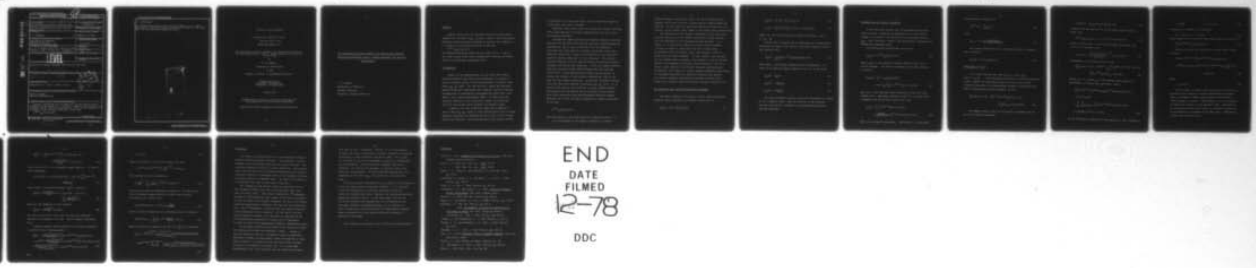

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The evaluation of matrix elements with generalized spherical Gaussian wavefunctions. Part I. Single particle, one- and two-centre forms.

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The evaluation of matrix elements with generalized spherical Gaussian wavefunctions. Part I. Single particle, one- and two-centre forms

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Abstract

General expressions are provided for the two-centre matrix elements for the unity (i.e., overlap), kinetic, and electrostatic potential energy operators evaluated in terms of the elements of a general set of Gaussian functions of the form

$$r^{2n+\ell}Y_{\ell m}(\hat{r})\exp(-\alpha r^2).$$

The formulae derived are valid for all orders of n, ℓ, and m. The single centre forms follow automatically from the two-centre forms in the vanishing separation limit.

Introduction

Because of the computational facility which they afford, Gaussian functions have been used increasingly in a number of areas of nuclear, atomic, and molecular physics (Moshinsky 1969, Hehre, et. al. 1969). For the most part, atomic and molecular quantum mechanical calculations have employed cartesian Gaussian wavefunctions or wavefunction transformations (Boys 1950, 1960, Shavitt 1963, Shavitt and Karplus 1965). In these cases the Gaussian integrals are all relatively simple; the analytical forms for the various matrix elements are equally simple.

In general, the most extensively used recent approach is that of Hehre et. al. (1969) in which minimal basis sets of simple spherical Gaussians are optimized to give a best fit to a single Slater-type function. The restricted basis sets usually consist

of functions all of the same order, but with differing expansion coefficients and orbital exponents.

Moshinsky (with Novaro 1968) has carried out several investigations using spherical oscillator eigenfunctions for light atoms and diatomic molecules.

Although the simple cartesian and simplest spherical Gaussian functions are the most often used for molecular quantum mechanical calculations, and in spite of the fact that new quadrature algorithms are being found for integral evaluations using these functions (King 1975), a case can be made for the use of general spherical Gaussian functions in some situations. The simplest Gaussian functions lack the nodal properties of the more accurate hydrogenic and Slater-type functions. In the last decade floating spherical Gaussian orbital (FSGO) methods have been explored (Frost 1967). These functions more readily and accurately reproduce the features of the accurate wavefunctions than is the case with the simplest functions. In addition, extended Gaussian basis sets have been examined (Ditchfield, et. al. 1971). It is possible that some of the attributes of these extended methods, particularly the FSGO method, may be contained within minimal basis sets constructed from the orthonormal spherical harmonic functions or at least in terms of generalized spherical Gaussians of the form

$$r^{2n+\ell} Y_{\ell m}(\hat{r}) \exp(-\alpha r^2).$$

Most calculations to date have used these functions with n = 0.

It is the purpose of this paper, therefore, to present

general formulae, valid to any order, for the two-centre matrix elements which arise typically in many-particle quantum mechanical analyses. In the limit of a vanishing separation between the two centres, the two-centre forms reduce to the single centre expressions.

The evaluation of the integrals presented in this paper and the next, makes use of the Fourier convolution theorem together with the transforms of the wavefunctions and operators. As a result, it is possible to express the various matrix elements in terms of expansion coefficients similar to those found by Moshinsky (1959) and Brody, Jacob, and Moshinsky (1960) together with the Talmi integrals. In some respects, and certainly for the simplest matrix elements, this approach is overly powerful. However, the treatment of the many-centre integrals in the next paper is much simpler in the Fourier transform representation. In addition, with respect to certain quantum mechanical calculations for molecules dissolved in a spatially disperse polar medium, the Fourier transform representation provides the most direct route to the required forms of the matrix elements (Schmidt 1977).

One electron, one- and two-centre matrix elements

The matrix elements of the unity, kinetic, and electrostatic potential energy operators are defined respectively by

$$S_{ab}(\underset{\sim}{R}) = \int d^3r\ \phi_a^*(\underset{\sim}{r})\phi_b(\underset{\sim}{r}-\underset{\sim}{R}) \qquad (1)$$

$$K_{ab}(\underset{\sim}{R}) = -\frac{1}{2}\int d^3r\ \phi_a^*(\underset{\sim}{r})\nabla^2\phi_b(\underset{\sim}{r}-\underset{\sim}{R}) \tag{2}$$

$$C_{ab}(R) = \iint d^3r_1 d^3r_2 \phi_a^*(\underset{\sim}{r}_1)(1/|\underset{\sim}{r}_2 - \underset{\sim}{r}_1|)\phi_b(\underset{\sim}{r}_2-\underset{\sim}{R}) \tag{3}$$

where R is the vector separation between the centres a and b: $\underset{\sim}{R} = \underset{\sim}{R}_a - \underset{\sim}{R}_b$.

Each of these integrals can be represented by an appropriate expression in terms of the Fourier convolution integral (Prosser and Blanchard 1962)

$$I_{ab}^N(\underset{\sim}{R}) = \frac{1}{(2\pi)^3}\int d^3k\ k^{2N}\ \overline{\phi}_a^*(\underset{\sim}{k})\overline{\phi}_b(\underset{\sim}{k})\exp(i\underset{\sim}{k}\cdot\underset{\sim}{R}) \tag{4}$$

where $\overline{\phi}(\underset{\sim}{k})$ is the Fourier transform of the wavefunction. In terms of the function $I_{ab}^N(R)$ defined by eqn (4), we can write

$$S_{ab}(\underset{\sim}{R}) = I_{ab}^0(\underset{\sim}{R}) \tag{5}$$

$$K_{ab}(\underset{\sim}{R}) = -\frac{1}{2}I_{ab}^1(\underset{\sim}{R}) \tag{6}$$

$$C_{ab}(\underset{\sim}{R}) = 4\pi I_{ab}^{-1}(\underset{\sim}{R}). \tag{7}$$

Our task, therefore, reduces to that of evaluating the integral in (4) in general terms. This we carry out in the following sections with specific reference to the generalized spherical Gaussian functions.

Wavefunctions and Fourier transforms

In the following analysis only the unnormalized Gaussian forms are used. Normalization appropriate to a given matrix element is dictated by the character of the operator involved, e.g., unity (overlap), kinetic, and electrostatic (Roothaan 1951, O-Ohata and Ruedenberg 1966).

The unnormalized wavefunctions are given by

$$\phi_{n\ell m}(\underset{\sim}{r}) = r^{2n+\ell} Y_{\ell m}(\hat{r}) \exp(-\alpha r^2) \tag{8}$$

where $Y_{\ell m}(\hat{r})$ is the spherical harmonic function and α is an orbital exponent. The Fourier transform of the above function is given by

$$\begin{aligned} \overline{\phi}_{n\ell m}(\underset{\sim}{k}) &= \int d^3r \; \phi_{n\ell m}(\underset{\sim}{r}) \exp(i\underset{\sim}{k}\cdot\underset{\sim}{r}) \\ &= 4\pi i^{\ell} Y_{\ell m}(\hat{k}) \int_0^{\infty} dr \; r^{2n+\ell+2} \exp(-\alpha r^2) j_{\ell}(kr) \end{aligned} \tag{9}$$

and $j_{\ell}(x)$ is the spherical Bessel function of the first kind (Arfken 1970). The radial integral in eqn (9) is a known form (Gradshteyn and Rhyzik 1965), and we can write

$$\begin{aligned} f_{n\ell}(k) &= \int_0^{\infty} dr \; r^{2n+\ell+2} \exp(-\alpha r^2) j_{\ell}(kr) \\ &= \frac{\sqrt{\pi} n! k^{\ell}}{2^{\ell+2} \alpha^{n+\ell+3/2}} L_n^{\ell+1/2}(k^2/4\alpha) \exp(-k^2/4\alpha). \end{aligned} \tag{10}$$

$L_n^m(x)$ is the Laguerre polynomial. Specifically, we shall need

the definition (Arfken 1970)

$$L_n^{\ell+1/2}(x) = \sum_{s=0}^{n} a_{n\ell s} x^s \tag{11}$$

with

$$a_{n\ell s} = (-1)^s \frac{\Gamma(n+\ell+3/2)}{(n-s)!\,\Gamma(s+\ell+3/2)\,s!} \,. \tag{12}$$

Our concise definition of the wavefunction Fourier transform now is given by

$$\overline{\Phi}_{n\ell m}(\underset{\sim}{k}) = 4\pi i^{\ell} Y_{\ell m}(\hat{k}) f_{n\ell}(k) \tag{13}$$

Evaluation of $I_{ab}^{N}(\underset{\sim}{R})$

It is clear from eqn (10) that $f_{n\ell}(k)$ is real: viz., $f_{n\ell}^{*}(k) = f_{n\ell}(k)$. In the following discussion, we let the quantities a and b signify the coordinate origins as well as the orbital exponents associated with wavefunctions located at these positions. Hence, expanding the notation somewhat, we write

$$I_{ab}^{N}(n\ell m, n'\ell' m'; \underset{\sim}{R}) = \frac{2}{\pi} i^{\ell-\ell'} \int d^3k \; k^{2N} f_{n\ell}(k) f_{n'\ell'}(k)$$

$$\times Y_{\ell m}^{*}(\hat{k}) Y_{\ell' m'}(\hat{k}) \exp(i\underset{\sim}{k}\cdot\underset{\sim}{R}) \,. \tag{14}$$

The angular terms in eqn (14) are readily evaluated with the use of the Rayleigh expansion

$$\exp(i\underset{\sim}{k}\cdot\underset{\sim}{R}) = 4\pi \sum_{L,M} i^L Y_{LM}(\hat{R}) Y^*_{LM}(\hat{k}) j_L(kR) \tag{15}$$

together with the special case of the Wigner-Eckart theorem (Rose 1957)

$$\int d\Omega\ Y^*_{\ell_3 m_3} Y_{\ell_2 m_2} Y_{\ell_1 m_1} = (\ell_1|\ell_3|\ell_2)(\ell_1\ell_2 m_1 m_2|\ell_3 m_3) \tag{16}$$

where $(\ell_1\ell_2 m_1 m_2|\ell_3 m_3)$ is the Clebsch-Gordqn coefficient, and $(\ell_1|\ell_3|\ell_2)$ is defined to be

$$(\ell_1|\ell_3|\ell_2) = \left\{\frac{(2\ell_1+1)(2\ell_2+1)}{4\pi(2\ell_3+1)}\right\}^{1/2} (\ell_1\ell_2 0\ 0|\ell_3 0). \tag{17}$$

Consequently, it is possible now to write

$$I^N_{ab}(n\ell m, n'\ell' m'; R) = 8i^{2m+\ell-\ell'} \sum_{L,M} i^L Y_{LM}(\hat{R})(\ell|L|\ell')(\ell\ell'-mm'|LM)$$
$$\times \int_0^\infty dk\ k^{2N+2} f_{n\ell}(k) f_{n'\ell'}(k) j_L(kR). \tag{18}$$

Define $L_m = \ell+\ell'$, where L_m is the maximum value assumed by L. Furthermore, it follows that $L_m \pm L$=even. Hence,

$$\int_0^\infty dk\ k^{2N+2+\ell+\ell'} L_n^{\ell+1/2}(k^2/4a) L_{n'}^{\ell'+1/2}(k^2/4b) \exp(-k^2(1/a$$
$$+ 1/b)/4) j_L(kR)$$
$$= \sum_{s=0}^{n} \sum_{t=0}^{n'} a_{n\ell s} a_{n'\ell' t} \int_0^\infty dk\ k^{2N+2+L_m+2} (k^2/4a)^s (k^2/4b)^t$$
$$\times j_L(kR) \exp[-k^2(1/a + 1/b)/4]. \tag{19}$$

In the following, we make use of the quantities z and A defined as

$$z = \sqrt{b/a}; \qquad A = (1+z^2)/4b. \tag{20}$$

In addition, a quantity p is defined by

$$2p = 2(s+t) + L_m - L = \text{even}, \tag{21}$$

which enables one to write the right hand integral in eqn (19) as

$$\int_0^\infty dk\ k^{2N+2p+L+2} j_L(kR)\exp(-Ak^2). \tag{22}$$

Consider the case for which N=0,1, and for which $2N+2p \geq 0$; one finds

$$z^{2s}(4b)^{-p+(L_m-L)/2}\int_0^\infty dk\ k^{2p+2N+L+2} j_L(kR)\exp(-Ak^2)$$

$$= 2^{2N+L_m+1}\sqrt{\pi}(p+N)!\, z^{2s} b^{-p+(L_m-L)/2} \zeta^{N+p+3/2}(\zeta R)^L L_{p+N}^{L+1/2}(\zeta R^2)$$

$$\times \exp(-\zeta R^2) \tag{23}$$

where

$$\zeta = b/(1+z^2). \tag{24}$$

At this point, we seek to make the analysis as concise as possible in the interest of future computational efficiency. Hence, we attempt to make as much contact with Moshinsky's (1969) methods as possible. Unfortunately, it is not possible to reduce this analysis to the Moshinsky-form. Nevertheless, it is possible to come close, and it is certainly possible to follow Moshinsky's treatment in the same sense. Consequently, we note that with the use of

$$L_{p+N}^{L+1/2}(0) = \frac{\Gamma(p+N+L+3/2)}{(p+N)!\,\Gamma(L+3/2)} , \tag{25}$$

in the limit as a=b=1/2 and R=0, the integral (23) reduces to

$$2^{L_m/2-p-1}\Gamma(p+N+3/2),$$

and all terms with L≠0 vanish. Therefore, we define

$$T_{pL}^{N}(R) = \frac{2^{2N+L_m+2}}{\Gamma(p+3/2)}\sqrt{\pi}(p+N)!\,b^{-p+(L_m-L)/2}\zeta^{N+p+3/2}(\zeta R)^{L}L_{p+N}^{L+1/2}(\zeta R^2)$$

$$\times\exp(-\zeta R^2). \tag{26}$$

This quantity is in effect a modified Talmi (1953) integral. In terms of this quantity, the double summation of eqn (19) can be written as

$$\sum_{s=0}^{n}\sum_{t=0}^{n'} a_{n\ell s}a_{n'\ell' t}\, z^{2s}\,\tfrac{1}{2}\Gamma(p+3/2)T_{pL}^{N}(R)$$

$$= \sum_{p} C(n'\ell',n\ell,L,p,z)T_{pL}^{N}(R) \tag{27}$$

with

$$C(n'\ell',n\ell,L,p,z) = \tfrac{1}{2}\Gamma(p+3/2)\sum_{s=0}^{n} a_{n\ell s}a_{n'\ell' p-s-(L_m-L)/2}\, z^{2s}. \tag{28}$$

The limits on the above p-summation in eqn (27) are

$$\tfrac{1}{2}(L_m-L) \le p \le \tfrac{1}{2}(L_m-L) + n + n'. \tag{29}$$

The C-coefficient reduces to the Moshinsky B-coefficient in the limit

$$\lim_{\substack{z\to 1\\ L\to 0}} C(n'\ell',n\ell,L,p,z) = \left\{\frac{\Gamma(n+\ell+3/2)\Gamma(n'+\ell'+3/2)}{4n!n'!}\right\}^{1/2} \times B(n'\ell',n\ell,p). \qquad (30)$$

The first term on the right hand side of (30) is the reciprocal of the product of spherical harmonic oscillator wavefunction normalization coefficients. The connection, eqn (30), between the C- and B-coefficients serves as a useful check.

It should be noted at this point that the C-coefficients are independent of N (which determines the type of matrix element) and R. Consequently, for a given, fixed set of orbital exponents (a, b, c, ..., etc.) one set of C-coefficients need be determined. The N- and R-dependencies are contained entirely in the modified Talmi integrals $T^N_{pL}(R)$.

The complete expression for the general matrix element under the condition $p+N\geq 0$ is

$$I^N_{ab}(n\ell m,n'\ell'm';R) = 8i^{\ell-\ell'}\frac{\pi n!n'!}{2^{\ell+\ell'+4}a^{n+\ell+3/2}b^{n'+\ell'+3/2}} \times \sum_{L,M} i^L(\ell|L|\ell')(\ell\ell'-mm'|LM)Y_{LM}(\hat{R})\sum_p C(n'\ell',n\ell,L,p,z)T^N_{pL}(R). \qquad (31)$$

This representation is not completely general, but it does encompass a great number of examples. It is concise and appears to be computationally efficient.

A general expression for $T^N_{pL}(R)$ can be derived. However, before presenting that formula, we consider the few limiting cases not included in eqn (26).

When p=0 and N=-1, $T^{-1}_{0L}(R)$ is given by the following:

$$T_{\theta L}^{-1}(R) = \frac{2}{\sqrt{\pi}}(4b)^{(L_m-L)/2}\int_0^\infty dk\ k^L j_L(kR)\exp(-Ak^2)$$

$$= \frac{2^L m_b^{(L_m-L)/2}}{R^{L+1}}\ \gamma(L+1/2,\zeta R^2) \qquad (32)$$

where $\gamma(L+1/2,\zeta R^2)$ is the incomplete gamma function. In terms of the relationship

$$\gamma(L+1/2,\zeta R^2) = \Gamma(L+1/2)\left\{\mathrm{erf}(\sqrt{\zeta}R) - \exp(-\zeta R^2)\sum_{s=0}^{L-1}(\zeta R^2)^{s+1/2} \times\frac{1}{\Gamma(s+3/2)}\right\} \qquad (33)$$

where erf(x) is the error function, $T_{0L}^{-1}(R)$ is given by

$$T_{0L}^{-1}(R) = \sqrt{\pi}\frac{(2\sqrt{b})^{L_m-L}}{R^{L+1}}(2L-1)!!\left\{\mathrm{erf}(\sqrt{\zeta}R) - \exp(-\zeta R^2) \times\sum_{s=0}^{L-1}\frac{(\zeta R^2)^{s+1/2}}{\Gamma(s+3/2)}\right\}. \qquad (34)$$

When L=0, the summation in (34) vanishes:

$$T_{00}^{-1}(R) = \sqrt{\pi}\frac{(2\sqrt{b})^{L_m}}{R}\ \mathrm{erf}(\sqrt{\zeta}R). \qquad (35)$$

Eqn (31) with eqn (26), (34), and (35) provides sufficient flexibility to compute any of the matrix elements considered here.

A general formula, which includes all the cases considered, is derived in the following manner.

$$T_{pL}^{N}(R) = \frac{2(4b)^{-p+(L_m-L)/2}}{\Gamma(p+N+3/2)}\int_0^\infty dk\ k^{2p+2N+L+2}j_L(kR)\exp(-Ak^2)$$

$$= (-1)^{p+N+1}\ \frac{2(4b)^{-p+(L_m-L)/2}}{\Gamma(p+N+3/2)}\ (d/dA)^{p+N+1}\int_0^\infty dk\ k^L j_L(kR)\exp(-Ak^2)$$

$$= \frac{\sqrt{\pi}2^{L_m-2p}\ b^{-p+(L_m-L)/2}}{R^{L+1}\Gamma(p+N+3/2)}\ (-d/dA)^{p+N+1}\gamma(L+1/2,R^2/4A). \qquad (36)$$

Let

$$x = R^2/4A \tag{37}$$

Then, the derivative in eqn (36) assumes the form

$$(-1)^{p+N+1}(2/R)^{2(p+N+1)}\left(x^2\,\frac{d}{dx}\right)^{p+N+1}\gamma(L+1/2,x)$$

The derivative can be expressed as

$$\left(x^2\frac{d}{dx}\right)^n = \sum_{s=0}^{n-1}\frac{n!}{(n-s)!}\binom{n-1}{s}x^{2n-s}(d/dx)^{n-s} \tag{38}$$

which can be proved by mathematical induction. The derivative of the incomplete gamma function to order m can be found with the use of (Arfken 1970)

$$(d/dx)^m[e^x\gamma(a,x)] = e^x\gamma(a-m,x)\frac{\Gamma(a)}{\Gamma(a-m)} \tag{39}$$

and the Leibnitz formula for the differentiation of a product:

$$(d/dx)^m\gamma(a,x) = \sum_{t=0}^{m}\binom{m}{t}(-1)^{m-t}\frac{\Gamma(a)}{\Gamma(a-t)}\gamma(a-t,x) \tag{40}$$

When the results are combined, eqn (41) for $T_{pL}^N(R)$ is obtained:

$$T_{pL}^N(R) = \frac{\sqrt{\pi}\,2^{L_m+2N+2}\,b^{-p+(L_m-L)/2}\,\Gamma(L+1/2)[(p+N)!]^{2(p+N+1)}}{R^{L+1}\,\Gamma(p+N+3/2)}$$

$$\times(\zeta R)^{2P+2N+2}\sum_{s=0}^{p+N}\sum_{t=0}^{p+N+1-s}\frac{(-1)^s\,\gamma(L+1/2-t,\zeta R^2)}{(\zeta R^2)^s[(p+N-s)!]^2 s!(p+N+1-s)\Gamma(L+1/2-t)} \tag{41}$$

Discussion

The analysis presented applies to the generalized spherical Gaussian functions defined by eqn (8). The treatment is easily extended to the orthonormal spherical oscillator functions. The resulting formulae are similar to those found here. This follows simply from the fact that the Fourier transform of the spherical oscillator function in coordinate space is an isomorphic spherical oscillator function in momentum space. The form of the function is essentially the same as that given by eqn (13).

The treatment of the general spherical Gaussians which we have presented differs from, and is more powerful than, that given by Harris (1963). Then, Harris handled the r^{2n}-dependence by means of differentiation with respect to the orbital exponent. For the two-centre, one electron integrals, the use of the Fourier transform representation eliminates the need for this differentiation. The r^{2n}-dependence is absorbed into the Laguerre function in the expression for the transform. For the three- and four-centre integrals, however, it is necessary to consider the use of differentiation operations to supress the r^{2n}-dependence at least for part of the manipulation (Schmidt, accompanying paper).

In this paper mention has been made of the connection between the techniques presented and Moshinsky's (1969). Indeed, as eqn (30) indicates, there is a reasonably close correspondence. Moshinsky's methods are particularly useful and powerful in those cases in which it is possible to use the same orbital exponent in each of the elements of the basis set. For a great many calculations, this is not the case, and the formalism presented

here must be used. Essentially, however, it is still possible to employ the spirit of Moshinsky's methods, especially as applied to molecular systems (Moshinsky and Novaro 1968). For a given set of values of the orbital exponents, a table of C-coefficients can be determined. The various matrix elements then can be evaluated. If a new set of exponents is required, then a new table can be constructed. For many practical calculations, the dimensions of the table (i.e., the array) are not excessively large.

We have not given consideration in this paper to the evaluation of the two-centre nuclear attraction integrals. It is possible within the framework of the analysis presented in the last section to include these forms. However, the resulting expressions depend upon infinite series. On the other hand, with the use of various rotations and translations to be considered in the next paper (Schmidt, accompanying paper), it is possible to obtain closed form, finite expressions for these matrix elements. Hence, consideration of the nuclear attraction integrals is deferred to that paper.

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